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13. ABSTRACT (Maximum 200 words) This represents the final report for two years of research at UCLA by the PI and her group on the gun tube erosion problem. In the past two years, they created new quantum-based simulation tools (both first principles and multiscale modeling techniques) and investigated surface, bulk, and interfacial materials aspects of the gun tube erosion problem. In brief, they developed: (i) two new versions of their spin-dependent pseudopotential theory that provides a more <i>ab initio</i> and more accurate description of magnetic transition metals such as Fe, (ii) a multiscale model that couples chemistry and mechanics to study hydrogen embrittlement in steel, and (iii) a scheme for calculating fracture energies of materials with mobile impurities (such as hydrogen in iron). They applied our spin-dependent pseudopotential theory to evaluate magnetism of vanadium surfaces, and applied density functional theory (DFT) to evaluate TiC and ZrC as possible protective coatings for steel. They also characterized via DFT the energetics and kinetics of how hydrogen and carbon adsorb and diffuse into iron, the structure and relative stability of cementite (iron carbide) surfaces, as well as predicting pathways for CO and H ₂ S adsorption, diffusion, and dissociation on Fe surfaces.				
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**“First Principles and Multiscale Modeling of
Spallation and Erosion of Gun Tubes”**

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Statement of the Problem Studied

Increasing the service lifetime of military machinery will improve logistics in the field (less down-time due to maintenance or replacement) and will free up resources for other pressing needs. To this end, the Army has a vested interest in enhancing the lifetime of gun barrels, which are limited currently by erosion of the steel from which the gun barrels are made. However, it is exceedingly difficult to determine experimentally *in situ* the mechanisms of erosion. Therefore, computer simulations can help elucidate those mechanisms and in ultimately extending the lifetime of gun barrels by discovering new ways to inhibit erosion.

In the past two years, we created new quantum-based simulation tools (both first principles and multiscale modeling techniques) and investigated surface, bulk, and interfacial materials aspects of the gun tube erosion problem. In brief, we developed: (i) two new versions of our spin-dependent pseudopotential theory that provides a more *ab initio* and more accurate description of magnetic transition metals such as Fe, (ii) a multiscale model that couples chemistry and mechanics to study hydrogen embrittlement in steel, and (iii) a scheme for calculating fracture energies of materials with mobile impurities (such as hydrogen in iron). We applied our spin-dependent pseudopotential theory to evaluate magnetism of vanadium surfaces, and applied density functional theory (DFT) to evaluate TiC and ZrC as possible protective coatings for steel. We also characterized via DFT the energetics and kinetics of how hydrogen and carbon adsorb and diffuse into iron, the structure and relative stability of cementite (iron carbide) surfaces, as well as predicting pathways for CO and H₂S adsorption, diffusion, and dissociation on Fe surfaces.

Summary of the Most Important Results

The most important findings during tenure of this grant are described below, where the references refer to the publication list at the end of this section. We begin by outlining the new methods we developed and then present major findings from our applications to gun tube erosion chemistry [12].

Development of Quantum-Based Simulation Tools for Condensed Matter

We discuss three advances in theoretical methods: (a) spin-dependent pseudopotential theory that gives an improved description of magnetic transition metals such as Fe and Cr present in the gun barrel; (b) cohesive theory of fracture for materials with mobile impurities; and (c) a quantum mechanically-informed continuum model of hydrogen embrittlement in metals.

A. Advances in Spin-Dependent Pseudopotential Theory

Since the primary components of a gun tube are steel and chrome, i.e. Fe and Cr, both of which are magnetic (Fe is ferromagnetic, Cr is antiferromagnetic), it is critical to describe their magnetic properties accurately, since these may affect other properties such as structure and energetics. The standard DFT pseudopotential method often fails to describe magnetic transition metals because the conventional pseudopotentials are spin-averaged. Our spin-dependent pseudopotential theory is constructed to give the correct pseudopotential limits for spin-neutral and fully spin-polarized atoms, and works between those limits by scaling the fully polarized potential by the spatially varying net spin polarization. It does so without added parameters, while providing a more flexible

description that self-consistently adapts to the local environment. We reformulated the theory to work in a plane-wave pseudopotential three-dimensionally periodic DFT code and showed that it yields superior descriptions of, e.g., bcc Fe and Cr compared to conventional norm-conserving pseudopotential DFT theory with little computational overhead [4]. We then applied this technique to a problem where conventional pseudopotential theory completely breaks down: the quenching of magnetism at the V(001) surface. We showed that our spin-dependent pseudopotential theory is as robust as all-electron methods, ably reproducing the magnetic quenching induced by the surface [6]. Most recently, we have reformulated the spin-dependent pseudopotential theory to work within the computationally advantageous ultrasoft pseudopotential formalism, showing that we retain the previously demonstrated accuracy of the norm-conserving approach, while dramatically lowering the cost of the calculation [16].

B. First Principles Fracture Energies for Materials with Mobile Impurities

One possible contributor to gun tube erosion is embrittlement of the steel by hydrogen. In order to develop a simulation tool for hydrogen embrittlement of steel, we first needed to characterize the extent of embrittlement as a function of hydrogen concentration. Therefore we needed to calculate, from first principles, the fracture energy of the metal in the presence of hydrogen. Defining the fracture energy according to the Griffith criterion for brittle fracture for a material whose composition distribution does not change with time is simple: it is twice the surface energy of the material. However, it is not obvious how to calculate fracture energies for materials where the composition is evolving in time, e.g., in the case of impurity diffusion. We proposed a scheme for calculating the fracture energy of a material with mobile bulk impurities via a Born-Haber cycle [9]. We showed that such a definition has the advantage of initial and final states at equilibrium, connected by well-defined and measurable energetic quantities, which can also be calculated from first principles. Using this approach, we calculated the ideal fracture energy of metals (Fe and Al) in the presence of varying amounts of hydrogen, using periodic DFT. We found that the metal ideal fracture energy decreases almost linearly with increasing hydrogen coverage, dropping by almost 50% at $\frac{1}{2}$ ML of hydrogen, indicating a substantial reduction of metal crystal cohesion in the presence of hydrogen atoms and providing some insight into the cohesion reduction mechanism of hydrogen embrittlement of metals.

C. A Quantum-Based Continuum Model of Hydrogen Embrittlement

While atomic level calculations can provide considerable insight, they are not directly comparable to experiments that measure fracture dynamics (e.g. crack propagation velocities, etc.). Working together with Michael Ortiz at Caltech, we constructed a multiscale model of hydrogen embrittlement in metals [11] based upon: (i) a cohesive law dependent on impurity coverage that is calculated from first principles; (ii) a stress-assisted diffusion equation with appropriate boundary conditions accounting for the environment; (iii) a static continuum analysis of crack growth including plasticity; and (iv) the Langmuir relation determining the impurity coverage from its bulk concentration. We considered the effect of yield strength, stress intensity factor, hydrogen concentration, and temperature. The calculations reproduce the following experimental trends: (i) initiation time and its dependence on yield strength and stress intensity factor; (ii) crack jump length at initiation; (iii) intermittent crack growth; (iv) crack growth thresholds and turnover and their dependence on yield strength; (v) the effect of the hydrogen concentration on the threshold stress intensity factor; and (vi) the effect of temperature on crack velocities at low temperature. The observed intermittent cracking can be

understood as being due to a time lag in the diffusion of hydrogen towards the cohesive zone, since a buildup of hydrogen is necessary in order for the crack to advance. The predictions are in good agreement with available measurements, suggesting that hydrogen-induced decohesion is a likely mechanism for hydrogen-assisted cracking in steel. This tool could be used, given initial conditions inside a gun barrel, to directly simulate hydrogen embrittlement of the steel gun barrel.

First Principles Characterization of Steel Carburization Mechanisms

Gun tube erosion starts with chemical degradation of steel. One possible contributing mechanism for gun tube erosion is carburization, in which excess carbon is incorporated into steel. The molecular source of this excess carbon is most probably CO, which is a propellant byproduct. It is thought that the carbon then diffuses into the steel and forms cementite, Fe_3C , which has been observed in eroded gun tubes by electron microscopy. It has been proposed that the considerably lower melting point of cementite may lead to melting and sweeping away of the melted material as part of the gun tube erosion mechanism.

We first carried out a study of bulk cementite and its low-index surfaces [1] using DFT within the generalized gradient approximation (GGA) for electron exchange and correlation; the latter is needed to properly describe bulk Fe. Seven low-index, stoichiometric (non-polar) surfaces of cementite were examined. The relative stability of these cementite surfaces correlates with surface smoothness: the more corrugated the surface, the higher the surface energy (the latter ranging between 2.0-2.5 J/m²). All but two of the cementite surfaces have surface energies lower than the most stable surfaces of pure iron. *This suggests that lower surface energies may also provide a driving force for formation of cementite near the surface of steel, leading to a surface on a gun tube that can melt at lower temperatures than steel and erode away.*

We then investigated the mechanism of carbon incorporation into iron, starting with adsorption, diffusion, and dissociation of CO [10], C adsorption and surface diffusion [14], and C diffusion into bulk Fe [3]. We predict that CO dissociation is more facile on Fe(100) than on Fe(110), because CO adsorbs lying down and highly activated on the more open (100) surface, while CO adsorbs linearly on the on-top site on the close-packed Fe(110) surface. For the latter, we predict that CO has to first move off the on-top site to a lying-down transition state; this produces a barrier of 1.5 eV compared to 1.1 eV on Fe(100), where the latter value is in excellent agreement with experiment [10]. After dissociation, O atoms remain on the surface while C atoms are embedded into high coordination sites on the Fe surfaces. In the subsurface region, carbon atoms prefer octahedral sites, as in bulk bcc Fe. Diffusion of carbon atoms into Fe(110) and Fe(100) subsurfaces involves barriers of 1.2 eV and 1.5 eV, respectively [14]. *We predict that the rate-limiting step for C incorporation into bulk Fe is CO dissociation on Fe(110) and is initial diffusion to subsurface sites on Fe(100).* The barrier for bulk C diffusion is considerably smaller than either of these steps, as we now discuss.

We find that the dissolution of carbon in bcc Fe is an endothermic process, with a predicted solution enthalpy of carbon in an octahedral site of 0.74 eV. This is consistent with the very low solubility of C in bcc Fe. *The barrier for carbon diffusion from one octahedral site to another (via a tetrahedral site) has a barrier of 0.86 eV, in excellent agreement with the experimental value of 0.87 eV [3].* This encouraging benchmark result prompted us to investigate carbon diffusion in austenite, whose electronic structure is less well-characterized experimentally. The calculated solution enthalpy is -

0.17 eV exothermic, consistent with the known greater solubility of C in austenite compared to ferrite. The diffusion barrier through austenite is calculated to be 0.99 eV. Since we model austenite with the FM high-spin phase, the diffusion barrier we obtain is not directly comparable to the experiments where austenite is usually paramagnetic. However, this prediction is relevant for C incorporation into Fe thin films, since FM high-spin fcc Fe can be obtained by epitaxial growth on an fcc metal substrate.

First Principles Characterization of Sulfidation and Hydrogen Incorporation in Steel

H₂S is a common byproduct of the propellants used in military guns and may be the source of the FeS observed by electron microscopy in eroded gun tubes, as well as the source of hydrogen that may cause hydrogen embrittlement of the steel. We calculated the energetics and mechanisms of H₂S reacting with Fe surfaces [13, 15] as well as the adsorption and diffusion of H atoms on [5], into and within [8] bcc Fe.

Generally, we found that on both Fe(110) and Fe (100), H₂S is weakly adsorbed (typically by ~0.5 eV) via a sigma-donor bond, HS is more strongly absorbed due to its ability to form a primarily ionic bond, and S is the most strongly bound of all due to its ability to form two polar covalent bonds. Diffusion barriers for H₂S to move across these surfaces are small (~0.1 eV). The minimum energy paths for H₂S and HS dehydrogenation involve rotating an H atom towards a nearby surface Fe atom, with the S-H bonds breaking on the top of one Fe atom. The barriers to break the S-H bonds in H₂S are very low (0-0.25 eV), suggesting deposition of S on Fe surfaces via H₂S is kinetically and thermodynamically facile [13, 15]. We also find that H can diffuse readily on Fe surfaces, with low barriers (e.g., <0.2 eV on Fe(110)) [5].

We then examined H absorption, dissolution, and diffusion energetics in bcc Fe, through both the Fe(110) and Fe(100) surfaces [8]. We find that H prefers to stay on the Fe surface instead of subsurfaces or in bulk. We find that it is endothermic to dissolve hydrogen into Fe, with hydrogen occupying tetrahedral sites over a wide range of concentrations. The endothermicity is consistent with the known low solubility of H in pure Fe. In the initial absorption step, we predict that H occupies a deep subsurface tetrahedral site for Fe(110) and a shallow subsurface tetrahedral site for Fe(100). Diffusion of H into Fe subsurfaces is predicted to have a much lower barrier for Fe(100) than Fe(110). Within bulk Fe, we predict that H diffuses through bcc Fe via a curved path between tetrahedral sites, with almost no activation barrier. We exclude an earlier proposed path via an octahedral site, due to analysis of the rank of the saddle point and its high barrier.

First Principles Exploration of Alternative Protective Coatings for Steel

In addition to examining failure mechanisms for gun tube erosion, we investigated possible alternative protective coatings for gun tubes. Currently, steel gun tubes are coated with chromium, which has two problems. One is that the Cr layer cracks and reactive gases reach the steel, leading to steel erosion. The second is that the electroplating process that produces Cr coating on steel unfortunately also produces carcinogenic Cr(VI), an environmental hazard. As a result, the Army is looking for alternative “green” (environmentally friendly) coatings. We considered ceramic materials as candidates, since ceramics have been used in other extreme environment conditions quite successfully to protect metal components. Ceramics generally exhibit low thermal conductivity and have high melting points, two very positive traits for this

application. In addition, we searched for ceramics that are very stable, do not undergo discontinuous phase transitions, have similar coefficients of thermal expansion to that of Fe, are narrow-range compounds (no variable composition), exhibit good mechanical properties, are environmentally friendly, and potentially adhere strongly to iron.

To this end, we examined the possible use of TiC and ZrC as protective coatings for steel [2, 7]. We did this by examining the interfaces formed between the most stable surfaces of TiC, ZrC [(100) for those two] and bcc Fe [(110) for Fe]. We find that both TiC and ZrC can form coherent, unreacted, low strain (~2%) interfaces with Fe. A mixture of metallic and covalent bonding controls the interfacial adhesion. Ultrathin layers adhere most strongly, where adhesion of > 3-4 ML leads to saturation of the interface adhesion at a lower bound. The interfacial adhesion for both carbides on iron is ~2.5 J/m², with TiC showing somewhat stronger adhesion. These coatings adhere quite strongly to Fe, though not as strongly as Cr does. TiC could be tried as a coating to see if it is useful. Of course, TiC may oxidize to titania; the question is to figure out the extent of oxidation and whether it is a problem. If so, then a protective oxide impermeable to oxygen such as alumina may have to be deposited on top of the carbide coating.

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Inventions

Development of the following algorithms and codes:

- Spin-dependent pseudopotentials in the Kleinman-Bylander form for use in both real and reciprocal space solid state density functional theory codes.
- Ultrasoft spin-dependent pseudopotentials generated on-the-fly within the CASTEP planewave DFT code.
- Multiscale model of hydrogen embrittlement of metals: includes stress-assisted diffusion, cohesive zone fracture mechanics, continuum plasticity (with Michael Ortiz)